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Infinite dilution sorption of C_7-C_{16} n-alkanes in original and thermally rearranged PI studied by inverse gas chromatography

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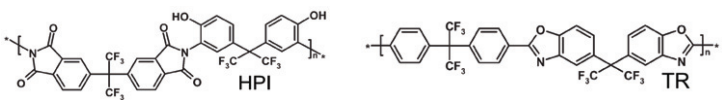
Thermal rearrangement of membrane materials has become one of the modern trends to improve their transport properties. In particular it was made for low permeable polyimide (PI). A gap in current knowledge regarding the reason for increases in gas permeability of such materials is the absence of the data on their sorption capacity and other thermodynamic properties.

Thus, the aim of this work was to investigate Inverse Gas Chromatography (IGC) the infinite dilution sorption of n-alkanes C_7-C_{16} in original polyimide with hydroxyl-groups (HPI) and its thermally rearranged product (TR) polybenzoxazole.



The original polymer was deposited on a macroporous support Inerton AW (0.16-0.20 mm) from its tetrahydrofuran solution (5 wt.%). The weight fraction of the polymer on the inert support was 9.3±0.1%. A half of the dried 'sorbent' was then heated according to the thermal treatment protocol used previously [1] (heating (5°C/min) up to 300°C, keeping for 1hr at this temperature, heating (5°C/min) up to 450°C, keeping for 1hr at this temperature and cooling to the ambient temperature) in an inert atmosphere of nitrogen. Sorption of n-heptane and n-octane in the original HPI was studied on a gas chromatograph with flame ionization detector in the temperature range 60-90°C whereas sorption of n-C_7, n-C_8, n-C_{10}, n-C_{12}, n-C_{14} and n-C_{16} solutes in TR polymer was investigated in the range 195-280°C. The rate of carrier gas (helium) was maintained at 5.0±0.2 cm^3/min over all experiments.

Retention diagrams (Fig. 1) of all the solutes in the both polymers were linear which indicated indirectly the absence of diffusion limitations during the IGC experiments. Extrapolation of the temperature dependencies of specific retention volume (V_g on Fig. 1) to 35°C allow us to calculate solubility coefficients of the solutes.

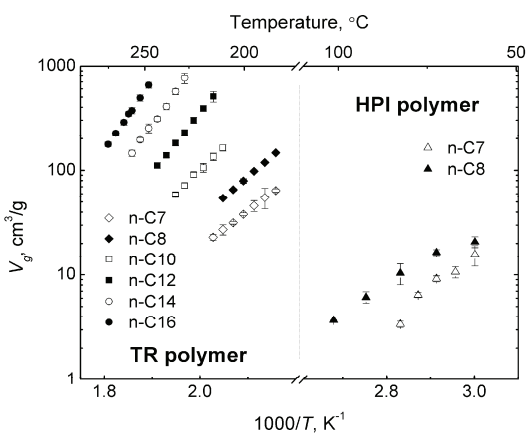


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Fig. 1. Retentions diagrams of n-alkane solutes in original HPI and TR polymers.

The solubility coefficients of n-heptane and n-octane in the original HPI were relatively low (Fig. 2). On the other hand, thermal rearrangement of it results in a thousand fold increase in solubility coefficients: the latter has as high solubility coefficients of n-alkanes as those in PIM-1 [2]. It can be reminded that PIM-1 is characterized by the highest gas solubility coefficients among other polymers studied. This indicates that the thermodynamic component of permeability (solubility) can play an important role in observed strong increases in gas permeability caused by thermal rearrangement.

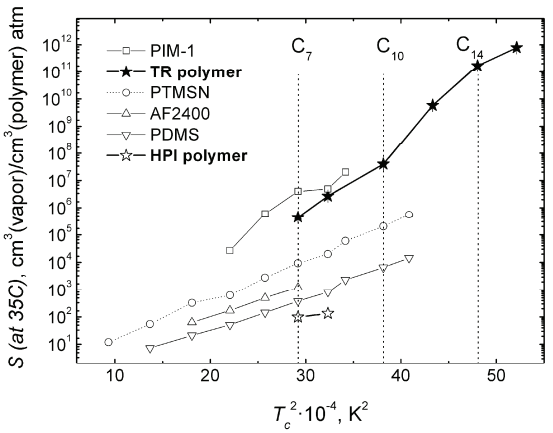

Fig. 2. Solubility coefficients of n-alkanes in highly permeable polymers vs. square of critical temperature. PIM-1 (polymer with intrinsic microporosity), PTMSN (additive poly(trimethylsilyl norbornene)), AF2400 (copolymer of tetrafluoroethylene and perfluoromethyldioxole), PDMS (polydimethylsiloxane).

Table. Thermal properties of sorption of several solutes in polymers studied by IGC

Polymer	U_1^S, kJ/mol		$h_1^{E,\infty}$, kJ/mol	
	n-heptane	n-octane	n-heptane	n-octane
HPI polymer (initial)	-46±10	-45±4	-18±10	-9±4
TR polymer	-66±1	-74±1	-38±1	-43±1
PIM-1	-69±1	-80±2	-27±5	-33±5
PTMSN	-49±1	-51±1	-21±2	-20±2

The IGC method allowed us to estimate the intrinsic energy of sorption U_1^S and excess partial molar enthalpy $h_1^{E,\infty}$. These values (Table) also reveal some differences in sorption of solutes in HPI and TR polymers. The intrinsic energies of sorption of C_7, C_8 alkanes in HPI are similar to intrinsic energies of condensation of these solutes, whereas U_1^S of the same solutes in TR polymer are much more negative. Moreover, while the dissolution of C_7, C_8 alkanes in the original HPI is only slightly exothermic, in the case of TR polymer, the excess enthalpies become strongly exothermic like in highly permeable, large free volume polymers such as PIM-1or additive PTMSN. This result is an indication of high fraction of excess free volume exists in the TR polymer.

References

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